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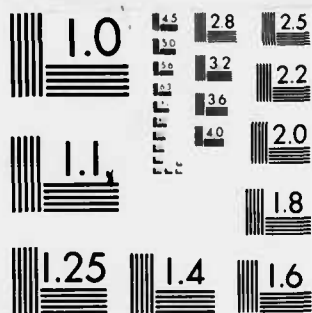
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Electron-Transfer Kinetics of Redox Centers Anchored  
to Metal Surfaces: Weak- Versus Strong-Overlap Reaction Pathways

by

S. W. Barr, K. L. Guyer, T. T-T. Li, H. Y. Liu and

M. J. Weaver

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Department of Chemistry

Purdue University

West Lafayette, IN 47907

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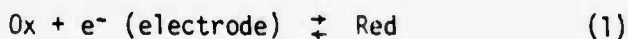
S.W. Barr, K.L. Guyer, T.T-T. Li, H.Y. Liu, and M.J. Weaver  
Department of Chemistry  
Purdue University  
West Lafayette, Indiana 47907

Abstract

Unimolecular rate constants  $k_{et}$  are presented for the one-electron electroreduction of various  $Co^{III}(NH_3)_5X$  complexes bound to mercury, platinum, and gold surfaces via either small inorganic or extended organic ligands X. These "surface intramolecular" rate parameters are compared with estimates of  $k_{et}$  for outer-sphere pathways obtained from homogeneous rate data in order to ascertain the consequences of reactant-surface binding upon the electron-transfer energetics. Only small or moderate decreases in the elementary reorganization barrier  $\Delta G_{et}^*$  occur upon surface attachment, suggesting the occurrence of weak-overlap pathways. Aside from the dependence of  $k_{et}$  upon the bridging ligand X at a given electrode potential due to differences in thermodynamic driving force, the observed variations in  $k_{et}$  appear to be due in part to variations in the electronic transmission coefficient  $k_{el}$ . Measurements of electrochemical frequency factors for reactants containing a series of thiophenecarboxylate bridges indicate that the substantial decreases in  $k_{et}$  observed upon interruption of ligand conjugation arise predominantly from decreases in  $k_{el}$ .

Although electrode processes commonly occur via reaction pathways involving specifically adsorbed intermediates, our understanding of the manner and extent to which the reaction-electrode interactions influence the electron-transfer energetics, i.e., determine the degree of electrocatalysis, is still at a rudimentary level. A difficulty that has hampered the elucidation of such "surface environmental" effects is that the reactions often occur via complex and/or uncertain mechanisms. One approach is to select for detailed study electrode reactions where the reactant, or reaction intermediate, is sufficiently strongly adsorbed to enable unimolecular rate constants ( $s^{-1}$ ) for the heterogeneous electron-transfer step to be evaluated in addition to the usual rate constants ( $cm\ s^{-1}$ ) for the overall reaction.<sup>1-3</sup> We have been interested in examining such systems that also are mechanistically simple, enabling detailed molecular-level interpretation of the rate data to be undertaken.

An especially tractable class of "model reactions" are one-electron transition-metal redox couples



where the solution species Ox and Red are substitutionally inert and bind strongly to the surface via a suitable coordinated ligand.<sup>1-3</sup> Such electrode reaction pathways can be labeled "inner sphere" by analogy with homogeneous electron-transfer processes between a pair of metal ions bound via a common ligand. Providing that the electron-transfer step is rate determining, the overall ("apparent") rate constant,  $k_{app}^{is}$  (cm s<sup>-1</sup>), for reaction (1) can be expressed simply as<sup>2-6</sup>

$$k_{app}^{is} = K_p^{is} k_{et}^{is} \quad (2)$$

where  $K_p^{is}$  is the stability constant for forming the adsorbed ("precursor") state from the bulk reactant, and  $k_{et}^{is}$  (s<sup>-1</sup>) is the rate constant for the elementary electron-transfer step involving the surface-attached intermediate. This "preequilibrium" treatment provides a convenient separation between electrocatalytic influences upon  $k_{app}^{is}$  arising from variations in the cross-sectional reactant concentration at the electrode surface, contained in  $K_p^{is}$ , and those due to variations in the electron-transfer energetics themselves, embodied in  $k_{et}^{is}$ .

Fundamental information on the surface environmental factors influencing  $k_{app}$  can therefore be obtained by examining separately the sensitivity of  $k_{et}^{is}$  as well as  $K_p^{is}$  to variations in the electrode composition and the structure of the bridging ligand.<sup>3-5</sup> We have demonstrated that a number of cobalt(III) and chromium(III) complexes are sufficiently strongly adsorbed at several metal surfaces, especially mercury, silver, platinum, gold, and copper, to enable values of  $k_{et}$  to be obtained for the one-electron reduction of the surface-bound redox center.<sup>2,3</sup> These complexes contain a simple inorganic (Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>) or an organic ligand (e.g. pyrazine, 4,4'-bipyridine, thiophenecarboxylates) featuring a halide, nitrogen, or sulfur lone pair as a surface "lead-in" group. These processes are closely analogous to the intramolecular reduction of Co(III) by homogeneous reducing centers such as Ru(II) and Fe(II) that have been extensively investigated in the last few years.<sup>7</sup> They therefore can be perceived as "surface intramolecular" reactions.

In this conference paper, we shall briefly present some of our recent results, chiefly for reductions of pentaamminecobalt(III), in order to illustrate the virtues of such strategies for unraveling the structural factors influencing the kinetics of electrocatalytic reactions. More complete descriptions of these results along with the experimental details are available elsewhere.<sup>2,3</sup>

#### Rate Formulations

Rate constants for surface-bound as well as other "intramolecular" reactions are related directly to the reorganization free energy for

the elementary electron-transfer step  $\Delta G_{et}^*$  by 6,8

$$k_{et} = \kappa_{el} \Gamma_n \nu_n \exp(\Delta G_{et}^*/RT) \quad (3)$$

The nuclear frequency factor  $\nu_n$  ( $\text{sec}^{-1}$ ) describes the effective frequency with which the configuration of the various nuclear coordinated appropriate for electron transfer is approached from the precursor state. The electronic transmission coefficient  $\kappa_{el}$  denotes the probability that electron transfer will occur once the transition state is reached. The nuclear tunneling factor  $\Gamma_n$  is a quantum-mechanical correction which accounts for the contribution to the measured rate from molecules which react without entirely surmounting the classical free-energy barrier.<sup>6,8</sup> Although  $\nu_n$  is a composite term arising from a weighted mean of manifold frequencies associated with reactant vibration and solvent reorientation modes, it will be close to  $1 \times 10^{13} \text{ sec}^{-1}$  for reactions, such as those considered here, where inner-shell reorganization provides an important component of  $\Delta G_{et}^*$ .<sup>6</sup> The nuclear tunneling factor  $\Gamma_n$  is usually close to unity (ca. 1-4) at room temperature. However,  $\kappa_{el}$  may well be orders of magnitude below unity if the electronic coupling between the donor and acceptor orbitals is weak (vide infra).

The reorganization energy  $\Delta G_{et}^*$  at a given electrode potential  $E$  can be separated into "intrinsic" and "thermodynamic" contributions:<sup>4</sup>

$$\Delta G_{et}^* = \Delta G_{int}^* + \alpha_{et} [RT(\ln K_p - \ln K_s) + F(E - E^\circ)] \quad (4)$$

Here  $\alpha_{et}$  is the transfer coefficient for the elementary step ( $\approx 0.5$ ),  $K_s$  is the equilibrium constant for forming the successor state (i.e. the ground state immediately following electron transfer) from the bulk product, and  $E^\circ$  is the standard potential for the redox couple. The "intrinsic barrier"  $\Delta G_{int}^*$  is the value of  $\Delta G_{et}^*$  that remains when the free energies of the precursor and successor states are equal.<sup>4</sup> It is of particular interest since it is the free energy barrier usually calculated from contemporary electron-transfer theories. The first and second sets of terms in parentheses in Eq (4) constitute "surface" and "bulk" components, respectively, of the thermodynamic driving force for the elementary electron-transfer step.

#### Consequences of Surface Attachment Upon Electron-Transfer Energetics

A central question in the examination of electrocatalytic reactions is to what extent the elementary barrier to electron transfer is modified by binding the reactant to the electrode surface. In view of Eq (3), the rate constant  $k_{et}$  for passage over this barrier may well be increased by surface attachment as a result of an increase in  $\kappa_{el}$  as well as from a decrease in  $\Delta G_{et}^*$ . Such variations in  $\kappa_{el}$  are characteristic of "weak overlap" reactions where the metal

redox center is almost entirely insulated from the electron donor (or acceptor) site provided by the electrode surface. On the other hand, variations in  $\Delta G_{et}^*$ , more specifically in  $\Delta G_{nt}^*$ , are characteristic of "strong overlap" reactions. Here  $\kappa_{el} \approx 1$  and the interaction with the electron donor (or acceptor) site is sufficient to significantly distort the reactant and product potential-energy surfaces in the intersection region so that the net free energy barrier is "rounded off",<sup>9</sup> thereby decreasing  $\Delta G_{nt}^*$  and increasing  $k_{et}$ .

At first sight, the question of the influence of surface attachment upon  $k_{et}$  may seem hypothetical since values of  $k_{et}$  cannot usually be measured directly for unattached reactants. Nevertheless, the preequilibrium rate formalism embodied in Eqs (2) and (3) also applies to outer-sphere pathways;<sup>6</sup> i.e. those where the reactant in the transition state is separated from the electrode surface by at least one layer of solvent molecules.<sup>10</sup> For such processes the precursor stability constant  $K_p^{OS}$  can be estimated from<sup>6</sup>

$$K_p^{OS} = \delta r \exp(-w_p/RT) \quad (5)$$

where  $w_p$  is the average work involved in transporting the reactant from the bulk solution to the reaction site (precursor state), and  $\delta r$  is the effective thickness of the reaction zone. The latter equals the effective distances from the plane of closest approach over which electron tunneling can occur with sufficient probability to contribute significantly to the observed rate. Although the typical values of  $\delta r$  are uncertain, it is probably within a factor of two of ca.  $1 \times 10^{-8}$  cm for structurally simple reactants.<sup>6</sup> The average work term  $w_p$  can simply be estimated from  $w_p = ZF\phi_r$ , where  $Z$  is the reactant charge number and  $\phi_r$  is the average potential at the reaction site. An essentially equivalent formalism to this "encounter preequilibrium" model has been employed recently for outer-sphere redox reactions in homogeneous solution.<sup>8</sup> Besides their practical value, such treatments are fundamentally more correct than the gas-phase collisional model which commonly has been employed for describing outer-sphere reactions.<sup>6</sup>

Admittedly, electrode reactions usually follow rate-dominating inner-, rather than outer-, sphere pathways for reactants featuring surface attachment sites. Consequently, apparent rate constants and hence values of  $k_{et}$  for outer-sphere pathways,  $k_{et}^{OS}$ , will be unobtainable, at least within the same surface environment for which values of  $k_{et}$  for inner-sphere pathways,  $k_{et}^{IS}$ , are determined. Nevertheless, the desired estimates of  $k_{et}^{OS}$  can be obtained by several routes as follows:

Method I: Suitable chemical modification of the electrode surface, such as the monolayer adsorption of iodide or an under-potential deposited (upd) metal, can eliminate the competing inner-

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sphere route, enabling  $k_{et}^{OS}$  to be obtained from the measured value of  $k_{et}^{OS}$ , provided that  $k_p^{OS}$  can be estimated from double-layer structural data.<sup>3a,11</sup>

Method II: At least relative values of  $k_{et}^{OS}$  at a given electrode potential  $E$  for a series of structurally related reactants may be obtained directly from the corresponding second-order rate constants,  $k_h$ , for their homogeneous reduction (or oxidation) with a suitable reagent (e.g.  $Ru(NH_3)_6^{2+}$ ) that constrains the reaction to occur by an outer-sphere pathway.<sup>6,3a</sup> Thus providing  $k_p^{OS}$  is approximately the same for each reactant,

$$(k_{et,1}^{OS}/k_{et,2}^{OS})_E = (k_{h,1}/k_{h,2})_R \quad (6)$$

where the subscripts 1 and 2 refer to a pair of reactants, and  $R$  refers to a fixed homogeneous coreactant. This relationship follows from the "weak overlap" model of Marcus and others,<sup>12</sup> and has been shown to apply to a number of reactions involving transition-metal complexes.<sup>11,13,14</sup> Additionally, if one or more of the electrochemical rate constants is known to refer to an outer-sphere pathway, Eq (6) can be utilized to obtain estimates of  $k_{et}^{OS}$  for the remaining members of the series.

Method III: For reactants where the surface attachment site is relatively remote from the redox center, such as for extended organic bridges,  $k_{et}^{OS}$  may be identified approximately with that obtained for a related reactant containing a similar ligand that lacks the surface-binding group.<sup>3c</sup>

Methods II and III will be utilized here. Various illustrative kinetic data for the one-electron reduction of fifteen  $Co^{III}(NH_3)_5X$  complexes (RoX) are gathered in Tables IA and B. With the exception of  $OH_2$ ,  $NH_3$ ,  $F^-$  and acetate ( $OAc^-$ ), all the ligands  $X$  feature a lone pair on a nitrogen, sulfur, or halide atom which induces sufficiently strong binding at suitable metal surfaces to enable the extent of reactant adsorption, and hence  $k_{et}^{IS}$ , to be measured. The values of  $k_{et}^{IS}$  given in Table I were obtained either from the corresponding apparent rate constants  $k_{app}^{IS}$  combined with  $K^{IS}$  [Eq (2)] or directly from the transient currents for reduction of the initially adsorbed species. Details are given elsewhere.<sup>2,3</sup> The precursor stability constant  $K^{IS}$  was determined from  $K^{IS} = \Gamma_p/C_b$  (cm), where  $\Gamma_p$  is the surface concentration (mole  $cm^{-2}$ ) in the precursor state at a given electrode potential, and  $C_b$  (mole  $cm^{-3}$ ) is the corresponding bulk reactant concentration. Mercury-, platinum-, and gold-aqueous interfaces were selected for detailed study of these reactions. The polarizable potential range at platinum and gold extends to sufficiently positive values to enable kinetic data to be obtained even for the most reactive complexes. The mercury-aqueous interface provides an especially suitable surface with which to obtain outer-,

as well as inner-, sphere rate data in view of its reproducibility and well-defined structure. The values of  $\Gamma_p$  were obtained primarily using rapid linear sweep voltammetry and, at mercury, by additionally using chronocoulometry.<sup>2,3</sup> The rate constants in Table I all refer to a common electrode potential, 0 mV vs. sce. This choice, although somewhat arbitrary, was made so to minimize the extent of data extrapolation that was involved. The relative values of  $k_{et}$  are approximately independent of the potential chosen.

Outer-sphere values of  $k_{et}^{os,Hg}$ , are listed in parentheses in Table I for the four  $Co^{III}(NH_3)_5X$  reductions,  $X = OH_2, NH_3, F^-,$  and  $OAc^-$ , expected to refer to outer-sphere electrochemical pathways at mercury electrodes. These were obtained from the apparent rate constants at mercury in  $NaClO_4$  and/or  $KPF_6$  electrolytes by using Eq (3) with  $\delta r = 1 \times 10^{-8}$  cm,  $w_p$  being estimated from the diffuse-layer potentials,  $\phi_r$ , as described in refs. 15 and 16.

Values of  $k_{et}^{os}$  are also given for most other reactions in Table I. These values, labelled  $k_{et}^{os,Ru}$ ,  $k_{et}^{os,Cr}$ , and  $k_{et}^{os,Fe}$ , refer to the homogeneous reduction of a given  $Co^{III}(NH_3)_5X$  complex by  $Ru(NH_3)_6^{2+}$ ,  $Cr(bpy)_3^{2+}$  ( $bpy = 2,2'$ -bipyridine), and  $Fe(CN)_6^{4-}$ , respectively.<sup>3,6</sup> They were obtained from the corresponding second-order rate constants for reduction of each complex relative to that for  $Co(NH_3)_5OH_2^{3+}$  reduction (Method II). The values of  $k_{et}^{os}$  were derived by combining these relative values of  $k_{et}^{os}$  with the estimate of  $k_{et}^{os,Hg}$  for  $Co(NH_3)_5OH_2^{3+}$  reduction, ca  $2 \times 10^3 \text{ sec}^{-1}$ , obtained at the mercury-aqueous interface at 0 mV vs sce. The validity of this procedure is supported by the approximate agreement (within ca. two fold) between the corresponding values of  $k_{et}^{os,Hg}$ ,  $k_{et}^{os,Ru}$ , and  $k_{et}^{os,Cr}$ , although somewhat larger differences in these quantities are seen for  $Co(NH_3)_5OAc^{2+}$  reduction (Table I).

Close examination of values of  $k_{et}^{is}$  and  $k_{et}^{os}$  reveals several interesting trends. Broadly speaking, the variations in  $k_{et}$  for the surface-attached reactants obtained by altering the bridging group X follow those for the corresponding values of  $k_{et}$  for outer-sphere homogeneous environments. This indicates that the reorganization barrier to electron transfer is not greatly altered by surface attachment via these bridging ligands. In other words, the substantially larger rate constants for the overall reaction at mercury,  $k_{app}^{Hg}$ , seen for reactions following ligand-bridged pathways (Table I) can be attributed in large part to the increases in  $K_p$ , i.e. the greater cross-sectional reactant concentrations at the electrode surface, brought about by reactant-surface bond formation.

Nevertheless, significant differences in  $k_{et}$  are seen for a number of reactants in the various reaction environments. Thus for  $X^- = NCS^-, Br^-,$  and  $Cl^-$ ,  $k_{et}$  differs by up to 100-fold between the corresponding values obtained for inner-sphere electrochemical, and outer-sphere homogeneous, reaction environments. The values of  $k_{et}^{os}$

are not expected to depend significantly upon the reaction environment. However, the homogeneous reductants  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Cr}(\text{bpy})_3^{2+}$  yield larger values of  $k_{\text{et}}^{\text{os}}$ , yet the reductant  $\text{Fe}(\text{CN})_6^{4-}$  yields smaller values than those of  $k_{\text{et}}^{\text{is}}$  obtained for the corresponding inner-sphere electrochemical pathway. Moreover, the values of  $k_{\text{et}}^{\text{is}}$  for  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  relative to those for  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  reduction at gold and platinum are 200 and  $2 \times 10^3$ , respectively; although comparable ratios of  $k_{\text{et}}^{\text{os}}$  are seen for  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Cr}(\text{bpy})_3^{2+}$  ( $4 \times 10^2$  and 75, respectively), the corresponding  $k_{\text{et}}^{\text{os}}$  ratio is only ca 6 for reduction by  $\text{Fe}(\text{CN})_6^{4-}$ . These results suggest that the reactant orientation can have an important influence upon  $k_{\text{et}}$ . Thus the anionic ligand  $\text{NCS}^-$  or  $\text{Cl}^-$  is anticipated to be oriented towards the cationic reductants  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Cr}(\text{bpy})_3^{2+}$ , but away from the anionic reductant  $\text{Fe}(\text{CN})_6^{4-}$ . However, "strong overlap" pathways are very unlikely for outer-sphere reactions. Therefore the much larger values of  $k_{\text{et}}^{\text{is}}$  for  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  relative to  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  reduction at gold and platinum may well be associated with the necessary orientation of anionic ligands towards the electrode, rather than any diminution of the reorganization barrier caused by binding the reactant to the metal surface.<sup>3a</sup> The origin of such orientation effects may lie in the increased orbital overlap, and hence larger values of  $\kappa_{\text{el}}$ , brought about by interposing chloride (or bromide) ligands between the donor and acceptor orbitals located at the metal surface and  $\text{Co}(\text{III})$ , respectively.

In order to more fully understand the effects of varying the bridging ligand X upon the intramolecular reactivity, it is necessary to estimate the variations in the thermodynamic driving force term  $[RT(\ln K_p - \ln K_s) + F(E - E^\circ)]$  in Eq (4). Although to a first approximation the "surface" component  $RT(\ln K_p - \ln K_s)$  can be neglected since we expect that  $K_p \approx K_s$ , at a given electrode potential the "bulk" driving force  $F(E - E^\circ)$  may vary greatly due to the dependence of the standard potential  $E^\circ$  on the ligand structure. Although values of  $E^\circ$  are largely unknown for the present  $\text{Co}(\text{III})/(\text{II})$  couples, information on the likely variations in  $E^\circ$  with X can be obtained as follows.

The variation in  $k_{\text{et}}$  relative to that for  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  reduction,  $k_{\text{et}}^{\text{OH}_2}$ , caused by variations in the driving force term  $F(E - E^\circ)$  can be expressed as

$$k_{\text{et}}^{\text{th}} = k_{\text{et}}^{\text{OH}_2} (K_{\text{II}}/K_{\text{III}})^{1/2} \quad (7)$$

where  $K_{\text{III}}$  is the equilibrium constant for  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{OH}_2 + \text{X} \rightleftharpoons \text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ , and  $K_{\text{II}}$  is the equilibrium constant for formation of the corresponding  $\text{Co}(\text{II})$  complex. Although values of  $K_{\text{II}}$  are unknown, they are expected to be in most cases smaller and markedly less dependent on X than are the values of  $K_{\text{III}}$  in view of the difference in electronic configuration between  $\text{Co}(\text{III})$  and  $\text{Co}(\text{II})$  ( $t_{2g}^6$  and  $t_{2g}^5 e_g^2$ , respectively). Therefore an approximate (and probably limiting) estimate of the expected driving force effects upon  $k_{\text{et}}$  can

be obtained by inserting the appropriate literature values of  $K_{III}$  into Eq (7), along with the experimental value of  $k_{et}^{OH_2}$ , taking  $K_{II}$  as a constant.

The resulting "thermodynamic" estimates of  $k_{et}^{th}$ ,  $k_{et}^{ec}$ , are also listed in Table IA. (The sources of  $K_{III}$  are given in the footnote to Table I. The value of  $K_{II}$  was taken as  $0.1 M^{-1}$ ; although somewhat arbitrary, this choice is intuitively reasonable given that Co(II) is expected to have some affinity for anionic ligands relative to  $H_2O$ , the value  $K_{II} \approx 0.02 M^{-1}$  corresponding to an absence of such affinity). Comparison of the values of  $k_{et}^{OS}$  and  $k_{et}^{IS}$  with the corresponding estimates  $k_{et}^{th}$  shows that the observed variations of  $k_{et}^{IS}$  as well as  $k_{et}^{OS}$  with the nature of X are in large part accounted for by this "thermodynamic" component, although the values of  $k_{et}$  for  $Co(NH_3)_5Cl^{2+}$  and  $Co(NH_3)_5Br^{2+}$  reduction in electrochemical ligand-bridged and cationic outer-sphere environments are somewhat larger than expected on this basis. We therefore conclude that binding Co(III) to the electrode surface via simple halide or pseudohalide ligands produces only relatively minor changes in the elementary electron-transfer barrier, although some "inner-sphere catalysis" does occur for chloride and bromide ligands at platinum and gold. The latter, nonetheless, may be due to increases in  $k_{el}$  caused by more favorable electronic coupling rather than to diminutions in  $\Delta G_{in}^*$  caused by the occurrence of "strong overlap" reaction pathways.

Turning now to the organic ligand-bridged reactions, comparison of  $k_{et}$  values for the seven thiophene-attached reactants in Table IB provide further evidence of the occurrence of electronic coupling effects. The  $k_{et}^{IS}$  values at mercury for the reactants featuring uninterrupted conjugation between Co(III) and the sulfur surface binding site are relatively constant ( $25-30 sec^{-1}$ ) and close to  $k_{et}^{OS}$  for  $Co(NH_3)_5OAc^{2+}$  reduction. However,  $k_{et}^{IS}$  for reactants containing one or more saturated carbons between the carboxylate group and the thiophene ring are 10- to 20-fold smaller (Table I). In contrast,  $k_{et}^{OS}$  for  $Ru(NH_3)_6^{2+}$  reduction of these complexes show only a relatively small dependence on the thiophenecarboxylate structure, the nonconjugated ligands yielding somewhat larger  $k_{et}^{OS}$  values than the conjugated systems. This indicates that the smaller  $k_{et}^{IS}$  values for the former systems at mercury are characteristic of the ligand-bridged mechanism itself, rather than to variations in the properties of the isolated Co(III) redox center such as the  $E^\circ$  values. The most likely explanation is that the electronic coupling between the Co(III) acceptor and surface donor orbitals is sufficiently weak for the nonconjugated ligands to yield smaller values of  $k_{el}$ , and hence smaller  $k_{et}^{IS}$  values [Eq (3)], than for the conjugated ligands. This is supported by the activation parameter data discussed below. The absence of further decreases in  $k_{et}^{IS}$  as the number of saturated carbons is increased from one to three may well be due to the involvement of an alternative reaction pathway where the electron tunnels "directly" between the surface and the Co(III) rather than via the bridging

ligand. Interestingly, these ligand conjugation effects are absent for the reduction of the surface-bound thiophene complexes at gold, the relative values of  $k_{et}^{is}$  following instead the  $k_{et}^{OS,Ru}$  values (Table I). One explanation is that the mode of adsorption of the bridging ligand at gold differs from that at mercury, the thiophene ring possibly lying flat or the carboxyl oxygen binding to the metal in the former case. This may enable reasonable electronic coupling to be maintained even in the absence of bridging ligand conjugation.

#### Activation Parameters for Surface-Bound Reactants

In addition to the evaluation of  $k_{et}^{is}$  at a single temperature, valuable information on the factors influencing the electron-transfer energetics for surface-bound reactants may be obtained from measurements of electrochemical activation parameters. We have recently discussed their significance for surface-bound reactants.<sup>17</sup> Since neither the standard potentials nor their temperature dependences are known with any accuracy for the present systems, so-called "ideal" activation enthalpies  $\Delta H_i^\ddagger$  were determined from Arrhenius plots of  $\ln k_{et}^{is}$  against  $(1/T)$  at a constant cell potential using a nonisothermal cell arrangement. These measurements enable the frequency factor for the elementary electron-transfer step,  $A_{et} [= \nu_n \kappa_{el} \Gamma_n]$ , Eq (3), to be determined from

$$\ln A_{et} = \ln k_{et}^{is} + \Delta H_i^\ddagger / RT - \Delta S_i^\ddagger / R \quad (8)$$

where  $\Delta S_i^\ddagger$  is the "ideal" activation entropy. Although  $\Delta S_i^\ddagger$  is not negligible it can be estimated from  $\Delta S_i^\ddagger = 0.5 \Delta S_{et}^\circ$ , where  $\Delta S_{et}^\circ$  is the entropic driving force ("reaction entropy") for the electron-transfer step. For the present Co(III)/(II) couples, on the basis of the available reaction entropy data<sup>18</sup>  $\Delta S_{et}^\circ$  is expected to lie in the range 20-30 e.u.

Values of  $\Delta H_i^\ddagger$  and  $A_{et}$  for reduction of selected surface-bound reactants at mercury electrodes are summarized in Table II. Since the estimated values of  $\Delta S_{et}^\circ$  have uncertainties in the range ca 5 - 10 e.u., the resulting frequency factors  $A_{et}$  may be up to 3 to 10-fold in error. Nevertheless, the relative values of  $A_{et}$ , particularly for structurally similar reactants, are more reliable. The two Cr(III) reactants both yield values of  $A_{et}$  that are close to the value,  $1 \times 10^{13} \text{ sec}^{-1}$ , expected for adiabatic pathways ( $\kappa_{el} \approx 1$ ) for which  $A_{et} \approx \nu_n$ . The  $A_{et}$  values for the two Co(III) reactants,  $\text{Co(en)}_2(\text{NCS})_2$  (I)<sup>n</sup> and  $\text{Co}(\text{NH}_3)_5(2\text{-thiophene acrylate})^{2+}$  (IV) (both  $1 \times 10^{12} \text{ sec}^{-1}$ ), suggest that these reactants are also close to being adiabatic ( $\kappa_{el} \approx 0.1$ ). However, the remaining thiophene complexes (V, VI, VII) which have interrupted conjugation exhibit markedly ( $10^2$  to  $10^3$ -fold) smaller values of  $A_{et}$  as well as  $k_{et}^{is}$ . This supports the above suggestion that the smaller reactivity of

these latter complexes arises from the weaker electronic coupling (i.e. smaller values of  $\kappa_{el}$ ) brought about by the interposition of saturated carbon atoms between the donor and acceptor sites.

### Conclusions

The foregoing analyses indicate that attachment of Co(III) to mercury, platinum, and gold surfaces via either simple inorganic or organic bridging groups yields only small or moderate changes in the elementary reorganization barrier  $\Delta G^*$ . Thus the corresponding values of  $k_{et}^{is}$  and of  $k_{et}^{os}$  obtained either in other reaction environments or estimated from the reactivities of structurally similar reactants are typically within ca. 5- to 30-fold of each other. In addition to the influence of the bridging ligand upon  $k_{et}$  arising from variations in the thermodynamic driving force, the dependence of  $k_{et}$  on the nature of the bridging ligand appears to arise in part from alterations in  $\kappa_{el}$  as a result of changes in the degree of electronic coupling between the surface donor and Co(III) acceptor orbitals. These reactions can therefore be considered to involve weak- rather than strong-overlap electron transfer. The possible exceptions are halide bridges at platinum and gold, where the surface bonds are expected to be relatively covalent, thereby weakening the Co(III)-halide bonds and decreasing the component of  $\Delta G^*$  and hence  $\Delta G_{in}^*$  associated with the inner-shell (metal-ligand) reorganization energy. However, the relatively large values of  $k_{et}^{is}$  observed for these reactions can be attributed in part to increases in  $\kappa_{el}$  arising from the enhanced electronic coupling provided by the interposition of the monoatomic ligand between the donor and acceptor orbitals.

The experimental frequency factors for the surface intramolecular reactions at mercury,  $A_{et} \approx 10^{10}$  to  $10^{13}$  sec<sup>-1</sup>, suggest that  $\kappa_{el}$  lies in the region ca  $10^{-3}$  - 1 (i.e. nonadiabatic pathways occur), although  $\kappa_{el}$  probably approaches unity (i.e. adiabaticity is achieved) with small inorganic bridging ligands. These conclusions are similar to those from recent experimental and theoretical work for related homogeneous electron-transfer processes. Thus values of  $\kappa_{el}$  substantially below unity are predicted for some homogeneous outer-sphere reactions even at small internuclear separations (5-6 Å).<sup>19</sup> Nonadiabatic pathways for homogeneous intramolecular Co(III) - Ru(II) reactions bridged by bipyridine ligands featuring interrupted conjugation are also evidenced by the values of  $A_{et}$  obtained for these processes,<sup>7</sup> especially after correction for the entropic driving force.<sup>20</sup>

It is interesting to compare this situation with the catalyses induced by the ligand-bridged reduction of  $Co^{III}(NH_3)_5X$  complexes by homogeneous reagents such as  $Cr^{2+}$ ,  $Eu^{2+}$ ,  $V^{2+}$ , and  $Fe^{2+}$ . The analysis of the reaction energetics is considerably more tenuous than for the electrochemical reactions since little information is available on the

precursor complex stabilities  $K_{15}^{\text{is}}$ . Moreover, the comparison of rate constants for corresponding outer- and inner-sphere pathways is less straightforward for homogeneous reactions since cognizance must be taken of the contribution to the reorganization energy from the coreactant. This component will probably be different for the outer- and inner-sphere routes since the coreactant's coordination sphere will necessarily be altered in forming the precursor complex.

Nevertheless, some useful deductions can be made from the available rate data. The most remarkable ligand-bridged rate accelerations occur for reductions by  $\text{Cr}^{2+}$ ; for example,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  is reduced by  $\text{Cr}^{2+}$  nearly  $10^{10}$  fold more rapidly than is  $\text{Co}(\text{NH}_3)_6^{3+}$ .<sup>21</sup> The corresponding rate ratios for reduction by  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$  are about  $10^4$ , similar to that for  $\text{Ru}(\text{NH}_3)_6^{2+}$  (Table I).<sup>21</sup> The  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ - $\text{Cr}^{2+}$  reaction clearly follows an inner-sphere pathway, whereas the latter two processes may follow outer-sphere mechanisms. Although the binding constant of  $\text{Cr}^{2+}$  to  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  is unknown, it would need to be ca  $10^6$ -fold higher than for the other reagents to account for the additional rate acceleration, which is highly implausible. Therefore this, and also other ligand-bridged  $\text{Co}(\text{III})(\text{NH}_3)_5\text{X}$  -  $\text{Cr}^{2+}$  reactions seem certain to occur via "strong overlap" pathways, i.e. where the elementary electron-transfer barrier  $\Delta G_{\text{et}}^{\ddagger}$  is lowered substantially by electronic interactions between the redox centers.<sup>4</sup>

There have been several recent discussions of the factors influencing such inner-sphere catalyses.<sup>22,23</sup> It suffices to note here that such rate enhancements appear to be dependent upon the symmetry of the donor and acceptor orbitals, the most dramatic rate accelerations occurring for systems where both orbitals have  $e_g$  symmetry.<sup>22</sup> For such systems, it has recently been suggested that the precursor formation and electron-transfer steps are merged such that the bridge forms a "three-center" bond with the two metal cations.<sup>23</sup> The absence of such dramatic catalyses for the electrochemical reduction reactions is probably related to the relatively weak electronic coupling expected between the surface and  $\text{Co}(\text{III})$   $e_g$  acceptor orbitals, although the donor orbitals at gold and especially platinum surfaces are expected to have some d orbital character. Nevertheless, strong-overlap electron transfer may well occur for electrochemical processes involving adsorbed redox centers, such as oxygen, which bind directly to metal surfaces rather than via a bridging group.

The evaluation of electrochemical rate constants and activation parameters for surface-bound reactants, especially for a series of structurally related systems, clearly provides detailed information on the electron-transfer energetics that are unavailable from measurements of electrochemical reactivities for bulk-phase reactants. We anticipate that a wealth of hitherto unavailable information on the factors influencing the degree of adiabaticity of heterogeneous electron-transfer reactions can be extracted from systematic studies of the dependence of  $A_{\text{et}}$  as well as  $k_{\text{et}}$  on the structure of the metal redox center, the metal surface, and the mediating group.

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



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TABLE IA. Unimolecular Rate Constants ( $s^{-1}$ ) for Reduction of  $Co(NH_3)_5X$  Complexes Containing Inorganic Bridging Ligands X at 0 mV vs sce in  $0.1M NaClO_4$

Reactant <sup>a</sup>	$\xrightarrow{b}$ Hg k <sub>app</sub> cm sec <sup>-1</sup>	Electrochemical <sup>d</sup> Hg k <sub>et</sub> is, Au k <sub>et</sub>	$\xrightarrow{e}$ is, Pt k <sub>et</sub>	$\xleftrightarrow{f}$ os, Ru k <sub>et</sub>	Homogeneous <sup>g</sup> os, Cr k <sub>et</sub>	$\xrightarrow{h}$ os, Fe k <sub>et</sub>	$\xrightarrow{i}$ th k <sub>et</sub>
$RoOH_2^{3+}$	$5 \times 10^{-4}$	$(2 \times 10^3)$		$[2 \times 10^3]$	$[2 \times 10^3]$	$[2 \times 10^3]$	$[2 \times 10^3]$
$RoNH_3^{3+}$	$1.5 \times 10^{-6}$	(10)		6			~10
$RoF^{2+}$	$2 \times 10^{-6}$	$(1 \times 10^2)$		200			~100
$RoAc^{2+}$	$2 \times 10^{-6}$	(80)		10	50	4	~50
$RoNCS^{2+}$	$3 \times 10^{-3}$	25	1.5	$5 \times 10^2$	$4 \times 10^2$	50	~30
$RoN_3^{2+}$	$3 \times 10^{-4}$	20 (~20)		$1 \times 10^3$	$1.5 \times 10^3$	25	~30
$RoCl^{2+}$	>0.1	$6 \times 10^3$	$3 \times 10^3$	$2 \times 10^5$	$3 \times 10^4$	$3 \times 10^2$	~ $5 \times 10^2$
$RoBr^{2+}$	>0.1	$8 \times 10^3$	$1.5 \times 10^3$	$1 \times 10^6$	$2 \times 10^5$		~ $1 \times 10^3$

For Table IB and footnotes, see following page.

TABLE IB. Unimolecular Rate Constants ( $s^{-1}$ ) for Reduction of  $Co(NH_3)_5X$  Complexes Containing Thiophenecarboxylate Bridging Ligands X at 0 mV vs sce in 0.1 M  $NaClO_4$

Reactant	Electrochemical		Homogeneous	
	$k_{app}^{Hg}$ $cm\ sec^{-1}$	$k_{et}^{Hg}$	$k_{et}^{is,Au}$	$k_{et}^{os,Ru}$
$RoOH_2^{3+}$	$5 \times 10^{-4}$	$(2 \times 10^3)$		$[2 \times 10^3]$
$RoAc^{2+}$	$2 \times 10^{-6}$	(80)		10
 $COORo^{2+}$	$2 \times 10^{-3}$	25	3	7
 $CH_2COORo^{2+}$	$4 \times 10^{-4}$	2.5	5	20
 $(CH_2)_2COORo^{2+}$	$6 \times 10^{-4}$	2.5	6	20
 $(CH_2)_3COORo^{2+}$	$3 \times 10^{-4}$	2	3	6
 $CH=CHCOORo^{2+}$	$3 \times 10^{-3}$	45	6	25
 $COORo^{2+}$	$5 \times 10^{-4}$	30	7	7
 $CH_2COORo^{2+}$	$5 \times 10^{-4}$	1.5	10	10

Footnotes to Tables IA and B.

<sup>a</sup> $Ro = Co^{III}(NH_3)_5$ , OAc = acetate.

<sup>b</sup>Apparent (measured) rate constant for overall reaction at mercury-aqueous interface measured using normal pulse or d.c. polarography.

<sup>c</sup>Unimolecular rate constant at mercury-aqueous interface. Values without parentheses,  $k_{et}^{is}$ , refer to inner-sphere (ligand-bridged) pathway, measured either directly or indirectly from  $k_{app}^{is}$  using Eq (2). Values within parentheses,  $k_{et}^{os}$ , refer to outer-sphere pathway at mercury, determined from  $k_{et}^{os} = k_{app}^{os} / k_{app}^{is}$ , with  $k_{app}^{os}$  determined from Eq (5) (see text).

<sup>d</sup>Value of  $k_{et}^{is}$  determined at gold-aqueous interface.

<sup>e</sup>Value of  $k_{et}^{is}$  determined at platinum-aqueous interface.

<sup>f</sup>Value of  $k_{et}$  for outer-sphere pathway,  $k_{et}^{os}$ , obtained from the value of  $k_{et}$  ( $2 \times 10^3\ sec^{-1}$ ) obtained for  $Co(NH_3)_5OH_2^{3+}$  reduction at mercury electrodes combined with relative rate constants for homogeneous reduction of  $Co(NH_3)_5X$  and  $Co(NH_3)_5OH_2^{3+}$  by  $Ru(NH_3)_6^{2+}$  [Eq (6)].

[continued over]

<sup>g</sup>As for footnote f, but using  $\text{Cr}(2,2\text{'-bipyridine})_3^{2+}$  as outer-sphere reductant.





<sup>h</sup>As for footnote g, but using  $\text{Fe}(\text{CN})_6^{4-}$  as outer-sphere reductant.

<sup>i</sup>Value of  $k_{\text{et}}$  determined from  $k_{\text{et}}^{\text{OH}_2}$  for  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  ( $2 \times 10^3 \text{ sec}^{-1}$ ) by correcting for changes in thermodynamic driving force ( $E-E^\circ$ ) using Eq (7), with  $K_{\text{II}}$  taken as 0.1 (see text).

Data Sources: All electrochemical rate data from refs. 3a-c. Homogeneous rate data for  $\text{Ru}(\text{NH}_3)_6^{3+}$  reductions:  $X = \text{OH}_2, \text{NH}_3, \text{Cl}^-, \text{Br}^-$ , J.F. Endicott, H. Taube, J. Am. Chem. Soc. 86, 1686 (1964);  $X = \text{F}^-$ , R.C. Patel, J.F. Endicott, J. Am. Chem. Soc. 90, 6364 (1968);  $X = \text{NCS}^-$ , N. A. Adegite, M. Dosumu, J.F. Ojo, J. Chem. Soc. Dalton, 630 (1977);  $X = \text{OAc}^-$ , thiophene carboxylates, ref. 3c. Rate data for  $\text{Cr}(2,2\text{'-bipyridine})_3^{2+}$  reductions: J.P. Candlin, J. Halpern, D.L. Trimm, J. Am. Chem. Soc. 86, 1019 (1964); Rate data for  $\text{Fe}(\text{CN})_6^{4-}$  reductions: D. Gaswick, A. Haim, J. Am. Chem. Soc. 93, 7347 (1971); A Mirralles, Ph.D. thesis, State University of New York at Stonybrook, 1974; A. Haim, personal communication.

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TABLE II. Electrochemical Activation Parameters for Reduction of Representative Surface-Bound Co(III) and Cr(III) Reactants at Mercury Electrodes in 0.1 M NaClO<sub>4</sub>.

Reactant	E mV vs sce	$k_{et}^{is}$ <sup>a</sup> sec <sup>-1</sup>	$\Delta H_i^*$ <sup>b</sup> kcal. mol <sup>-1</sup>	$\Delta S_i^*$ <sup>c</sup> cal.deg <sup>-1</sup> mol <sup>-1</sup>	$A_{et}$ <sup>d</sup> sec <sup>-1</sup>
I) c-Co(en) <sub>2</sub> (NCS) <sub>2</sub> <sup>+</sup>	-100	0.15	20.5	~10	~1x10 <sup>12</sup>
II) c-Cr(OH <sub>2</sub> ) <sub>4</sub> (NCS) <sub>2</sub> <sup>+</sup>	-600	70	20	~13	~3x10 <sup>13</sup>
III) f-Cr(OH <sub>2</sub> ) <sub>3</sub> (NCS) <sub>3</sub>	-600	70	16	~ 0	~3x10 <sup>13</sup>
IV)  -CH=CHCOORo <sup>2+</sup>	-200	4x10 <sup>3</sup>	15.6	~13	~1x10 <sup>12</sup>
V)  -CH <sub>2</sub> COORo <sup>2+</sup>	-200	260	14.1	~13	~1x10 <sup>10</sup>
VI)  -(CH <sub>2</sub> ) <sub>2</sub> COORo <sup>2+</sup>	-200	290	14.8	~13	~3x10 <sup>10</sup>
VII)  -(CH <sub>2</sub> ) <sub>3</sub> COORo <sup>2+</sup>	-200	230	13.2	~13	~1x10 <sup>9</sup>

<sup>a</sup>Unimolecular rate constant for reduction of surface-bound Co(III) or Cr(III) complex at stated electrode potential E.

<sup>b</sup>"Ideal" activation enthalpy at stated value of E, determined from  $\Delta H_i^* = R[\partial \ln k_{et} / \partial (1/T)]_E$  using a nonisothermal cell arrangement.<sup>17</sup>

<sup>c</sup>Estimated "ideal" activation entropy  $\Delta S_i^*$  (see text).

<sup>d</sup>Frequency factor for elementary electron-transfer reaction, determined from listed values of  $k_{et}^{is}$ ,  $\Delta H_i^*$ , and  $\Delta S_i^*$ .

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$X^- = \text{NCS}^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$ ,  $k_{\text{et}}$  differs by up to 100-fold between the corresponding values obtained for inner-sphere electrochemical, and outer-sphere homogeneous, reaction environments. The values of  $k_{\text{et}}^{\text{OS}}$

in electronic configuration between Co(III) and Co(II) ( $t_{2g}$  and  $t_{2g} e_g$ , respectively). Therefore an approximate (and probably limiting) estimate of the expected driving force effects upon  $k_{et}$  can

smaller  $k_{et}^{15}$  values [Eq (3)], than for the conjugated ligands. This is supported by the activation parameter data discussed below. The absence of further decreases in  $k_{et}^{15}$  as the number of saturated carbons is increased from one to three may well be due to the involvement of an alternative reaction pathway where the electron tunnels "directly" between the surface and the Co(III) rather than via the bridging

being adiabatic ( $k_{et} \approx 0.1$ ). However, the remaining  
complexes (V, VI, VII) which have interrupted conjugation exhibit  
markedly ( $10^2$  to  $10^3$ -fold) smaller values of  $A_{et}$  as well as  $k_{et}$ .  
This supports the above suggestion that the smaller reactivity of